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(54) **Colloidal composition for clarifying a fermented beverage**

(57) The composition comprises pectin having a molecular size range indicated by a limiting viscosity number less than 0.5, preferably from 0.005 to 0.2, such composition being obtained by depolymerisation of a natural pectin with pectinase at e.g. 30-60°C for from 1-4 days. The modified pectin may also be partially de-esterified by treatment with dilute alkali. The natural pectin may be an apple, citrus, beet, carrot, potato or sunflower pectin. The composition may also include a small quantity of isinglass and may be used in the fining of ales, beers, lagers and wines or low alcohol derivatives thereof.

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Colloidal compositions and their use
in the clarification of aqueous liquids.

This invention relates to colloidal compositions and to the use of the compositions in the clarification of aqueous liquids. The use of the compositions for the fining of beverages produced by fermentation, such as ales, beers, lagers or wines or low alcohol or alcohol-freed derivatives of these is within the ambit of the present invention although the invention is not limited to this. The term "fining" is used to indicate the removal of haze from a liquid such as, for example, the beverages mentioned above, by the addition of a suitable treatment agent to produce a product of acceptable clarity for consumption.

In the production of fermented beverages, after the separation of the main body of yeast, it is necessary to achieve the clarification of the remaining beverage to a high standard. While in the case of some wines acceptable clarification may occur over an extended period of time, in the case of ales and lagers it may be necessary to achieve rapid clarification so as to achieve a short storage time and rapid delivery of the product to the consumer. The clarification of fermented beverages may be conducted in clarification tanks, where the product is to be bottled or canned, or in the cask in the case of some ales which are dispensed directly.

The haze in fermented beverages is due to the presence of protein and tannin molecules as well as residual yeast cells and without the addition of a fining agent this haze may be slow to clear. Isinglass has traditionally been used as a fining agent, possibly in conjunction with auxiliary fining agents. Isinglass is derived from the swim bladders of certain species of fish and contains collagen. The collagen has a positively charged structure and sediments slowly entrapping negatively charged yeast cells and proteins as it does so. This may reduce the number of yeast cells in suspension in the main body of the liquid from up to about $2 \times 10^6/\text{ml}$ to less than about $1 \times 10^3/\text{ml}$. The auxiliary fining agents may be silicates or polysaccharides. These materials have a negatively charged structures and help to increase the electrostatic attraction between protein molecules and the isinglass thereby encouraging the sedimentation of these molecules. In the case of cask ales the sedimentation is destroyed each time the cask is moved and fining agents are preferably capable of causing repeated re-sedimentation without the need to use such a quantity of fining agent that an unduly large volume of "bottoms" forms in the cask.

According to one aspect thereof the present invention more particularly relates to a composition of matter comprising pectin and to its use as a new or improved clarification or fining agent.

Pectins are polysaccharide materials having gelation properties which are found in variable amounts in the primary cell walls and intercellular tissues of land plants. They are most abundant in fruit and vegetables, especially in the rinds of citrus fruits and apples and in beets, carrots and potatoes and in sunflower heads. British Patent No 555089 describes the production of pectinic acid salts by the hydrolysis of pectin using, for example, a solution of N/15 or N/30 NaOH at 15.55°C (60°F) for 12 or 15 minutes. Further hydrolysis is inhibited by back-titration to pH 7.5 or thereabouts. The effect of this hydrolysis is to de-esterify at least a proportion of the methoxyl side groups on the pectin molecule without causing

appreciable depolymerisation. When a solution of the pectinic acid salts so produced having a 0.5% pectin content was used as a fining agent for beer the quantity which was sufficient to achieve fining was 1.04% vol.(3 pints/barrel) for low gravity beers but 2.08% vol.(6 pts./barrel) for all gravity beers. The Applicant is unaware of any current commercialisation of such a product as a fining agent.

The present invention provides a composition of matter, suitable for use as a fining agent, and also a process for fining using the composition, the composition being characterised in that it comprises pectin having a molecular size range indicated by a limiting viscosity number (hereafter LVN) of less than 0.5. LVN is measured according to Atkins (Physical Chemistry, 2nd. Ed., pages 825 to 827 using a U-tube viscometer. Preferably the pectin has a LVN of less than 0.4, particularly preferably less than 0.3, for example no more than 0.2. Preferably the pectin has a LVN of at least 0.005, for example at least 0.01. Such a composition, when in the form of an aqueous solution of a concentration suitable for use as a fining agent, has been found to be effective in comparison with commercially available pectins, such as apple or citrus pectins, which can have a natural LVN about 0.6 and have little or no fining activity either in their normal state or when de-esterified.

The present invention also provides a process for the production of a fining agent according to the invention comprising modifying pectin by depolymerising it into the LVN range stated above. This makes possible the use of commercially available pectins, for example fruit pectins such as apple or citrus pectins, or root or tuber pectins such as beet, carrot or potato pectins, or sunflower pectin, after suitable modification according to the invention, as effective fining agents.

The pectin may be modified according to the invention by exposure to the action of the enzyme pectinase. The pectin is preferably treated with the pectinase in the form of an aqueous

solution of about 1% to 10% by weight concentration of pectin. The pectinase is preferably present in about 0.01% to 1% by weight. The solution is preferably held at above-ambient temperature, for example at from 30°C to 60°C, for from 1 to 4 days. The precise conditions, concentrations etc. are selected to achieve the required LVN, for example, very suitably, an LVN of from 0.01 to 0.2.

Preferably the modified pectin according to the invention is also de-esterified to a degree of esterification of less than 50%, particularly preferably less than 30%, for example, very suitably, less than 25%. There may be residual esterification of, for example, up to 10% or more. De-esterification is preferably achieved by treatment with dilute alkali, for example as disclosed in British Patent No 555089 referred to above. Preferably the de-esterification is conducted on the already modified pectin.

The susceptibility of different liquids requiring fining to the action of the fining agent according to the invention may vary. In general, effective fining action may be obtained using the fining agent, added at a concentration of from about 0.5% to 2% and/or in a quantity of from about 0.17% to 1.04% vol. (0.5 to 3 pints/barrel), or at a concentration or quantity outside those ranges, the concentration or quantity being selected to be appropriate for the particular beer or lager, or other beverage or liquid. In some cases a small quantity of isinglass may additionally be used. Auxiliary fining agents may also be used but are not usually necessary.

The invention will now be illustrated by reference to the following non-limiting examples thereof and, for comparative purposes, to examples of the use of fining agents outside the invention. Tests 2 to 5, 7 to 10, 13, 14, 16 to 18 and 20 to 51 are examples according to the invention and the remaining tests are comparative tests outside the invention.

The effect of pectinase on the molecular size of samples of pectin was examined by adding a selected quantity of pectinase in the range 0.001% to 0.5% by weight, as the product Pectinol (Pectinol is a Trademark), to a colloidal dispersion of pectin in water at a concentration selected in the range 0.5% to 5% by weight and maintaining the dispersion at a temperature of 20°C or 40°C for a given time. Hereafter stated % proportions of these materials are weight % unless otherwise stated. In most cases the resulting dispersion of modified pectin was de-esterified by the addition of 0.5% by weight of NaOH, added as a 1 molar solution and the maintenance of the dispersion at a temperature of 20°C for 30 minutes. Unless otherwise stated the pectin used in the following tests had been de-esterified after the pectinol treatment. The pectin dispersion was then examined as to its LVN, by the method referred to above, or as to its fining effect on one of a variety of beers and lagers. The fining effect was judged by the following tests.

(A) Haze after a given time.

Measured using a Radiometer haze meter and expressed in Formazin haze units.

(B) Sediment % after 1 or 3 days

The height of the sediment was expressed as a % of the total height of the liquid.

- (C) Visual tests. i Visual observation of the formation of flocs and their sedimentation to leave a clear supernatant liquid (yes/no)
- ii Visual assessment according to Institute of brewing method (A,B etc.)

Certain tests were also carried out on pectin before modification, with or without de-esterification, and on pectinol itself to establish that it did not contribute to the fining effect.

Tests on Pectinol.

It was determined that Pectinol had no fining activity (Test Ci) at 0.5% concentration whether subjected to the de-esterification treatment or not.

Tests on apple and citrus pectins.

Samples of apple pectin having a degree of esterification of 59-64%, or citrus pectin having a degree of esterification of 68-72%, gave no fining activity (Test Ci) as 0.5% dispersions. Apple pectin which had been de-esterified gave no fining activity as a 1% dispersion.

Effect of Pectinase on LVN

Samples of apple pectin having a degree of esterification of 59-64% as such, and after treatment with Pectinol at 0.05% by weight and at 20°C and 40°C for various periods of up to 4 days, followed by de-esterification according to the method described in British Patent no. 555089, were tested for LVN. The results are as follows.

Table 1 (Tests 1 to 5)

Test	LVN
1 Pectin - no Pectinol treatment	0.595
2 Pectinol 20°C for 46 hours	0.200
3 " 40°C " " "	0.146
4 " 20°C " 4 days	0.100
5 " 40°C " " "	0.060

Similar tests on citrus pectin having a degree of esterification of 68-72% gave the following results.

Table 2 (Tests 6 to 10)

Test	LVN
6 Pectin - no Pectinol treatment	0.620
7 Pectinol 40°C for 6 hours	0.085
8 " 20°C " 46 "	0.035
9 " 20°C " 4 days	0.020
10 " 40°C " 46 hours	0.020

In tests for fining activity (Ci) of the same apple pectin which had been subjected to treatment with Pectinol at 40°C for 2 days successful fining was achieved where the pectin had a concentration of 1% with a pectinol concentration of only 0.01% and above but where the pectin had a concentration of 5% a Pectinol concentration of 0.025% gave some degree of fining while fully successful fining was achieved at a Pectinol concentration of 0.05% and above, in each case after de-esterification.

Tests were carried out to compare the fining activity of a pectin which had depolymerised to an LVN of 0.105 with isinglass and auxiliary fining agents. The tests for fining activity were visual clarity (Cii) and sediment weight (B). The quantities of fining agent are stated in % vol. as conversions from pints/barrel.

Table 3 (Tests 11 to 23)

Tests 11 to 14, 15 to 18 and 19 to 23 were performed on different bitter beers (cask).

Test	Cii	B%
11 Isinglass 1.04% + auxiliary 0.347%	B	2
12 " 1.388%+ " "	A	2
13 Depolymerised pectin 1.04%	B	3
14 " " " + aux 0.347%	A	5
15 Isinglass 0.694% + auxiliary 0.347%	A	2
16 Depolymerised Pectin 0.17%	C	1-2
17 " " 0.347%	B	2
18 " " 0.694%	A	3
19 Isinglass 1.388% + auxiliary 0.347%	A	3
20 Depolymerised pectin 0.17%+isin.0.17%	B	4
21 " " 0.17%+isin.0.347%	A	6
22 " " 0.086%+isin.0.347%	A	3
23 " " 0.694%	E	5

"Isin" is used to indicate isinglass. The use of the composition of the present invention in combination with isinglass in the fining of liquids is an advantageous feature of the invention.

Tests were carried out on the fining efficiency, in relation to another commercial beer and a lager, of apple or citrus pectin which has been subjected to varying degrees on depolymerisation by treatment with pectinase. The results are summarised in the following Tables 4 and 5 in which Column "a" identifies the Test Number, Column "b" the pectin source, columns "c" and "d" the duration, in hours or days, and temperature, in Degrees Centigrade, of the treatment of the pectin with the pectinase Pectinol and columns "e" to "h" the Haze and Sedimentation test results after 1 day or 3 days of fining.

Table 4
Tests performed on a lager beer.

a	b	c	d	e	f	g	h
Test No.	Pectin Source	Pectinol Temp	Time	Haze	1Day Sed%	3 Days Haze	Sed%
24	Apple	20C	3Hr.	8.3	1	2.9	1
25	Apple	20C	6Hr.	7	2	2.8	1
26	Apple	20C	46Hr.	6	3	2.4	2
27	Apple	20C	3Days	6	3	2.2	2
28	Apple	20C	4Days	5.4	2	2.2	1
29	Apple	40C	3Hr.	5.6	3	2.4	1
30	Apple	40C	6Hr.	5.2	2	2.2	1
31	Apple	40C	18Hr.	5.6	3	2.4	1
32	Apple	40C	46Hr.	5.1	3	2.3	2
33	Apple	40C	4Days	4	2	2.3	2
34	Citrus	20C	3Hr.	5.5	3	2.4	2
35	Citrus	20C	6Hr.	6.4	3	2.5	1
36	Citrus	20C	46Hr.	4	3	2.3	2
37	Citrus	20C	3Days	3.1	3	2	2
38	Citrus	20C	4Days	2.7	3	1.9	2
39	Citrus	40C	3Hr.	4.9	2	2.5	2
40	Citrus	40C	6Hr>	4.3	3	2.3	2
41	Citrus	40C	18Hr.	3.4	3	2	2
42	Citrus	40C	46Hr.	3.9	2	2.1	2
43	Citrus	40C	4Days	4.8	2	2.4	2

Table 5

Tests performed on bitter beer

a	b	c	d	e	f
Test No.	Pectin Source	Pectinol Temp	3 Days Time	Haze	Sed%
44	Apple	20C	3Hr.	3.1	7
45	Apple	20C	6Hr	3.1	8
46	Apple	20C	46Hr.	2.8	9
47	Apple	20C	4Days	2.6	10
48	Apple	40C	6Hr.	2.9	9
49	Apple	40C	18Hr.	3.1	9
50	Apple	40C	46Hr.	3.3	10
51	Apple	40C	4Days	2.5	9

Claims.

1. A composition suitable for use as a fining agent the composition being characterised in that it comprises pectin having a molecular size range indicated by a limiting viscosity number less than 0.5.

2. A composition as claimed in claim 1 wherein the pectin has a molecular size range indicated by a limiting viscosity number less than 0.2.

3. A composition as claimed in claim 1 or 2 wherein the pectin has a molecular size range indicated by a limiting viscosity number of at least 0.005.

4. A composition as claimed in any preceding claim wherein the pectin is derived from apple, citrus, beet, carrot, potato or sunflower.

5. A composition as claimed in any preceding claim wherein the pectin has a degree of esterification of at least 10% but less than 50%.

6. A process for fining an aqueous liquid comprising contacting the liquid with a composition as claimed in any preceding claim.

7. A process as claimed in claim 6 wherein the liquid is a beer, ale, lager, wine or a derivative of any of these.

8. A process for the production of a composition as claimed in any one of claims 1 to 5 comprising contacting pectin with pectinase under conditions suitable to attain a limiting viscosity number of at least 0.005 but less than 0.3.

9. A composition as claimed in claim 1 or a process for fining as claimed in claim 6 substantially as described herein with reference to any one of examples 2 to 5, 7 to 10, 13, 14, 16 to 18 and 20 to 51.



Application No: GB 9613698.1
Claims searched: 1-9

Examiner: L.V.Thomas
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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): A2B (BMH24); C3U (UCD); C6E (EJCA, EJCC, EJCD)
Int CI (Ed.6): A23L; C12H 1/02, 1/04, 1/10, 1/12, 1/14
Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0552728 A1 (Japan Tobacco) see p.3 ll.1-2 and 34-35, p.4 ll.9-10 and p.5 ll.37-54	1,4
X	US 4820520 (Yokotsuka et al.) see col.1 ll.50-54, col.2 ll.36-63 and col.3 ll.11-26	1,4
X	WPI Abstract Acc. No. 94-010974/02 & JP 5316997 A (Pola Chem.) see abstract	1,4,6,7

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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